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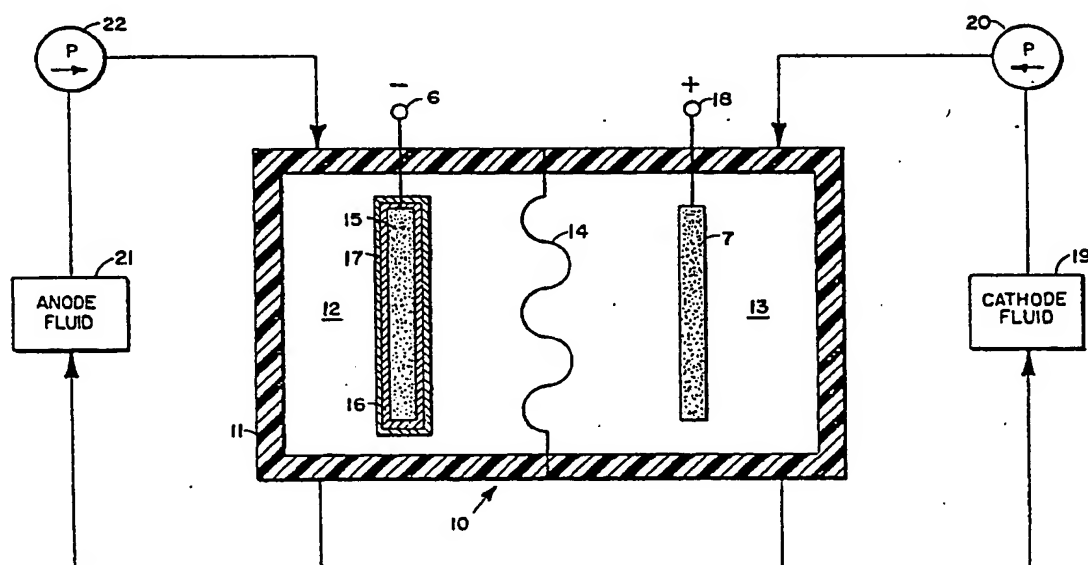
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With international search report

(54) Title: CATALYTIC SURFACE FOR REDOX CELL ELECTRODE



(57) Abstract

An electrical storage cell (10) of the reduction oxidation (REDOX) type is divided into anode and cathode compartments, (12 and 13), by a membrane (14), each compartment having a circulating fluid containing an ion couple for producing an electric potential at respective solid inert electrodes (7 and 15) disposed therein. The anode electrode (15) is plated with one layer (16) of copper, silver or gold and another layer (17) of lead or cadmium. The metal layers (16 and 17) provide an electrochemically active surface for the reduction and oxidation activity of the cell which dramatically increases the current density at the electrodes.

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Catalytic Surface for REDOX Cell ElectrodeOrigin of the Invention

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435, 42 USC 2457).

Technical Field

This invention relates to electrical energy storage devices and particularly relates to electrically rechargeable reduction-oxidation (REDOX) flow cell systems.

A need exists for storing bulk quantities of electrical power obtained from intermittent or random sources such as wind-driven generators, and solar cells.

15 Pumped water storage systems wherein water from a water storage pond at one level is directed to a water storage pond at a lower level through a hydro-electric plant having a water pumping capability has proven to be a viable method of energy storage. Unfortunately, such facilities are limited to areas where the terrain is suitable for providing water sources at different elevations.

A number of other methods have been considered including the storage of compressed air in large reservoirs, flywheels, capacitive storage, inductive storage and a number of electrochemical schemes. Electrochemical storage batteries are generally expensive.



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Electrically rechargeable REDOX flow cell systems are well known and have a very high overall energy efficiency as compared to other systems. REDOX type cells also can be discharged more completely than secondary
5 battery systems. Additionally, REDOX cells are inexpensive as compared to secondary batteries and do not deteriorate as significantly when repeatedly discharged and recharged.

Background Art

10 U.S. Patent No. 3,996,064 is useful background for the understanding of the present invention. In that patent an electrically rechargeable REDOX flow cell is disclosed wherein an electric potential is obtained between electrodes disposed respectively in an anode fluid
15 having a chromic/chromous couple and a cathode fluid having a ferrous/ferric couple. The anode and cathode fluids are separated by an ion selective membrane. The electrodes are both disclosed as comprised of porous graphite products which are inert to electrochemical re-
20 action with the anode and cathode fluids while promoting the REDOX reaction on their surfaces.

Statement of Invention

It is an object of the invention to provide a REDOX cell which will deliver much greater current for any
25 given electrode surface area than prior art devices. It is another object of the invention to provide a REDOX type cell which will deliver an increasingly greater percentage of current when compared to prior art REDOX cells as the cell approaches a discharged condition.



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In accordance with the invention, catalytic coatings are provided on the surface of the anode electrode to enhance the reduction and oxidation activity of the desired ions in the fluid. In the preferred embodiment a thin
5 metal layer of copper, silver or gold and another layer of lead are deposited respectively on the anode electrode. In the iron/chromium fluid system of the preferred embodiment, the lead surface enhances the chromium reduction during the charging of the cell and produces a
10 60-fold increase of reduction current density over an untreated electrode.

When the REDOX cell is being discharged, the lead also functions very well as a surface for the reversible electrochemical oxidation of the chromous ions to chromic
15 ions, however, the lead itself also undergoes electrochemical oxidation and is depleted from the anode surface.

The thin metal layer of copper, silver or gold, which becomes exposed to the anode fluid, provides an
20 electrochemically active surface for the rapid oxidation of the chromous ions, and at the same time is less subject to being oxidized than the lead. The copper produces a 50 fold increase in current density and the gold and silver both produce about a 90 fold increase
25 over plain carbon electrodes. During the recharging process, the lead is replated onto the layer of copper, silver or gold and is again available to promote the reduction activity of the chromic ions.



Brief Description of the Drawings

FIG. 1 is a cross-sectional view of the REDOX cell embodying the invention showing the anode and cathode fluid supply systems schematically.

5 FIG. 2 is a graph illustrating the increased current density in a REDOX cell embodying the invention.

FIG. 3 is a graph illustrating current density versus potential for different electrode materials.

FIG. 4 illustrates current density versus potential for a carbon electrode with a catalytic coating and
10 utilizing desired ions in the fluid to plate out on the coated electrode.

Best Mode for Carrying Out the Invention

Referring now to FIG. 1, there is shown a REDOX cell 10 comprising container 11, divided into compartments 12 and 13 by an ion conductive membrane 14. The graphite electrode 15 is disposed in the chamber 12 and connected to an output terminal 6 while a graphite electrode 17 is disposed in compartment 13 and connected to an output terminal 18. Electrode 15 in the anode compartment 12 is
20 coated with metal layers 16 and 17 to be more fully described hereinafter.

As shown, a cathode fluid from a cathode fluid source 19 is circulated by a pump 20 through compartment 13. Similarly, anode fluid from an anode fluid source 21
25 is circulated by a pump 22 through the compartment 12.



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In a preferred embodiment the REDOX cell 10 utilizes an iron/chromium system wherein the cathode fluid contains a ferrous/ferric couple while the anode fluid contains a chromic/chromous couple. Both fluids are acidified solutions between 1 and 4 molar. The anode fluid preferably contains water and HCl (aqueous solution of HCl) having dissolved therein a chromium chloride salt whereby cations in a reduced state are produced. The cathode fluid likewise is water and HCl but has dissolved therein an iron chloride salt whereby cations in an oxidized state are produced. These fluids provide the desired couples in each of the chambers 12 and 13. A more complete discussion of the couple, the fluid and electrode requirements and membrane considerations is given in U.S. patent No. 3,996,064 which is incorporated herein by reference.

While the REDOX cell herein has been described as using an anode fluid having an chromous/chromic couple and a cathode fluid having a ferrous/ferric couple, other couples may be used as indicated in the aforementioned patent. For example, titanium chloride may be used in the anode fluid to produce the cations in the reduced state and vanadium chloride or manganese chloride may be used in the cathode fluid to produce the cations in the oxidized state.

In accordance with the present invention, it has been found that a coating of lead on the inert electrode substantially increases the current density of the electrode, and consequently, the current available at terminals 6 and 18. This results from the fact that chromic reduction has been found to occur very rapidly on the



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lead surface. At the same time lead is also representative of a class of non-noble metals that possess a very high hydrogen over voltage, which advantageously results in a minimization of the rate of hydrogen evolution to preserve the electrical balance of the fluids.

Although lead chloride is discussed herein, it is noted that cadmium chloride may be substituted for or used in combination with lead chloride. Cadmium chloride achieves the same results as lead chloride in increasing catalytic activity of a carbon electrode for the reduction of chromic chloride with the simultaneous inhibition of hydrogen evolution.

On a lead surface which was prepared by the electrodeposition of a very thin layer of lead onto a smooth carbon rod, the reduction current was measured to be 12 ma/cm² at an electrode potential of -600 millivolts (mv) versus a standard calomel electrode (SCE). Under like conditions, the reduction current for an untreated electrode was only 0.2 ma/cm². Thus, the lead coating on a carbon rod provided a 60-fold increase of reduction current.

Referring now to FIG. 2, there is shown graphically the relative performance obtained over a wide range of potentials of a solution that contained no lead ions and one that contained 10⁻⁴ molar of lead ions.

The lead layer may be coated onto the electrode before it is disposed in chamber 12 to be contacted by the circulating anode with fluid. The lead layer may also be obtained by simply dissolving lead chloride in the anode fluid before charging the REDOX cell and al-



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lowing the lead, which is subject to anodic dissolution, to plate onto the electrode structure during the charging mode of the chromous/chromic reaction.

As mentioned previously, each time the REDOX cell is discharged, the lead is depleted from the anode by electrochemical oxidation and redissolved in the anode fluid. Because the carbon and graphite material of the electrode structure does not provide an active surface for the oxidation of the chromous ions, a further aspect of the invention is the provision of metal layer 17 as an electrochemically active surface between the lead layer and the electrode surface for this purpose. Metal layer 17 may be selected from the group comprising copper, silver and gold which have all been found to be electrochemically active surfaces for the rapid electrochemical oxidation of chromous ions, and at the same time, are less subject to being electrochemically oxidized than lead. FIG. 3 graphically illustrates the current density versus potential for silver, copper and smooth carbon surface. As shown, at an electrode potential of -550 mv versus a saturated calomel electrode the rate of electrochemical oxidation of a chromous ion is less than 0.1 ma/cm². Under the same conditions, the current produced by the silver surface is about 9 ma/cm² which is about a 90-fold increase. A copper surface under the same conditions yields 5 ma/cm² which is a 50-fold increase over a smooth carbon surface.

Referring now to FIG. 4, there is graphically shown the current density obtained for various electrode potentials for the chromous/chromic couple where the anode electrode is coated with gold and wherein lead chloride is dissolved in the anode fluid to provide lead



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ions. With the gold coating on the anode electrode it will be seen at negative 550 mv. versus the saturated calomel electrode the current for the electro oxidation of chromous ion is 9 ma/cm². This is a 90-fold increase over a plain carbon electrode.

The metal coating of silver, gold or copper on the inert electrode is very thin and may be applied by various procedures including electrodeposition, metal spraying, dipping or the like. The amount of metal in the coating is on the order of only a few molecular layers. A graphite felt was produced with 25 micrograms of gold per cm² of projected area. This provided suitable electrode performance during discharge. The lead coating which goes over the silver, gold or copper coating on the inert electrode, whether applied before the electrode is inserted in the anode chamber or by deposition from the anode fluid, can also be as thin as several monolayers, where a monolayer is one molecule in thickness.

The gold, silver and copper catalysts which enhance the oxidation of chromous ions during the discharge cycle may also be dissolved in the anode solution as salts to provide in-situ activation of the anode electrode. They can also be incorporated into the negative carbon electrode by saturating the electrode with a salt solution of gold, silver or copper followed by heat treatment to dry it.

It will be understood that changes and modifications may be made to the above described inventions by those skilled in the art without departing from the spirit and scope of the invention as set forth in the claims appended hereto.



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Claims

1. A REDOX cell having first and second chambers separated by an ion permeable membrane including:
an anode fluid in the first chamber;
5 a cathode fluid in the second chamber;
an anode electrode in said first chamber, said electrode being electrically conductive but inert with respect to the anode fluid;
a cathode electrode in said second chamber, said
10 electrode being electrically conductive but inert with respect to the cathode fluid;
said anode electrode having a coating of one or more metals deposited thereon to provide a surface which will act as a catalyst for electrochemical reduction
15 and oxidation activity during charging and discharging of said REDOX cell.
2. The REDOX cell of claim 1 wherein said metal coating deposited on the anode electrode includes a layer selected from the group of lead or cadmium.
- 20 3. The REDOX cell of claim 2 wherein said metal coating deposited on the anode electrode includes a layer of metal selected from the group of silver, gold and copper disposed between the surface of said anode electrode and said layer of lead or cadmium.
- 25 4. The REDOX cell of claim 3 wherein each layer of metal is 2-5 monolayers thick.



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5. A REDOX cell having first and second chambers separated by an ion permeable membrane including:
an anode fluid in the first chamber;
a cathode fluid in the second chamber;
5 an anode electrode in said first chamber, said electrode being electrically conductive but inert with respect to the anode fluid;
a cathode electrode in said second chamber, said electrode being electrically conductive but inert
10 with respect to the cathode fluid;
said anode electrode having metal deposited thereon selected from the group consisting of lead or cadmium.
6. The REDOX cell of claim 5 wherein the amount of metal
15 is 10^{-4} to 10^{-5} M/liter of anode fluid.
7. The REDOX cell of claim 6 wherein a metal layer selected from the group of silver, gold and copper is disposed between the anode electrode and the layer of lead or cadmium.
- 20 8. A REDOX cell having first and second chambers separated by an ion permeable membrane;
an anode fluid in the first chamber;
a cathode fluid in the second chamber;
an anode electrode in said first chamber, said electrode being electrically conductive but inert with
25 respect to the anode fluid;
a cathode electrode in said second chamber, said electrode being electrically conductive but inert with respect to the cathode fluid;



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said anode fluid having a metal chloride salt dissolved therein whereby the metal ions of said salt plate onto the anode electrode during the operation of said cell to provide a surface for catalyzing electrochemical activity of said cell.

9. The REDOX cell of claim 8 wherein said metal chloride salt is lead chloride or cadmium chloride or a combination of both.
10. The REDOX cell of claim 9 wherein said metal chloride salt is in the amount of 10^{-4} to 10^{-5} M/liter.
11. The REDOX cell of claims 8, 9 or 10 wherein a layer of metal selected from the group consisting of copper, silver and gold is disposed between said metal layer formed by said metal chloride salt.
- 15 12. The REDOX cell of claims 11 wherein said metal layer of copper, silver or gold is 2 to 5 monolayers thick.
- 20 13. A method of making a REDOX cell of the type having anode and cathode fluids including: the steps of dissolving a metal chloride salt selected from the group consisting of lead chloride and cadmium chloride to the anode fluid and then charging the cell to plate the metal ions of said salt onto an electrically conductive inert electrode disposed in the anode fluid.
- 25 14. The method of claim 13 wherein the metal ions produced in said fluid by said metal chloride salt are in the amount of 10^{-4} to 10^{-5} M/liter of anode fluid.



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15. The method of claim 13 wherein the electrode to be inserted in the anode fluid is first coated with a metal selected from the group consisting of silver, gold and copper.
- 5 16. The method of claim 15 wherein said metal coating is from about 2 to about 5 monolayers thick.
- 10 17. The method of claim 13 wherein a porous inert electrode to be disposed in the anode chamber is first saturated with a solution of a salt selected from the group consisting of gold chloride, silver chloride and copper chloride and then heat treated.
- 15 18. A method of making a REDOX cell of the type having anode and cathode fluids comprised of water and metal chloride salts and including the step of coating a metal selected from lead or cadmium onto an electrically conductive inert electrode before disposing the electrode in the anode fluid.
- 20 19. The method of claim 17 and including the additional step of providing the inert electrode with a coating selected from the group of metals consisting of silver, gold and copper before applying the lead coating.
20. The method of claim 19 wherein each coating is from about 2 to about 5 monolayers thick.



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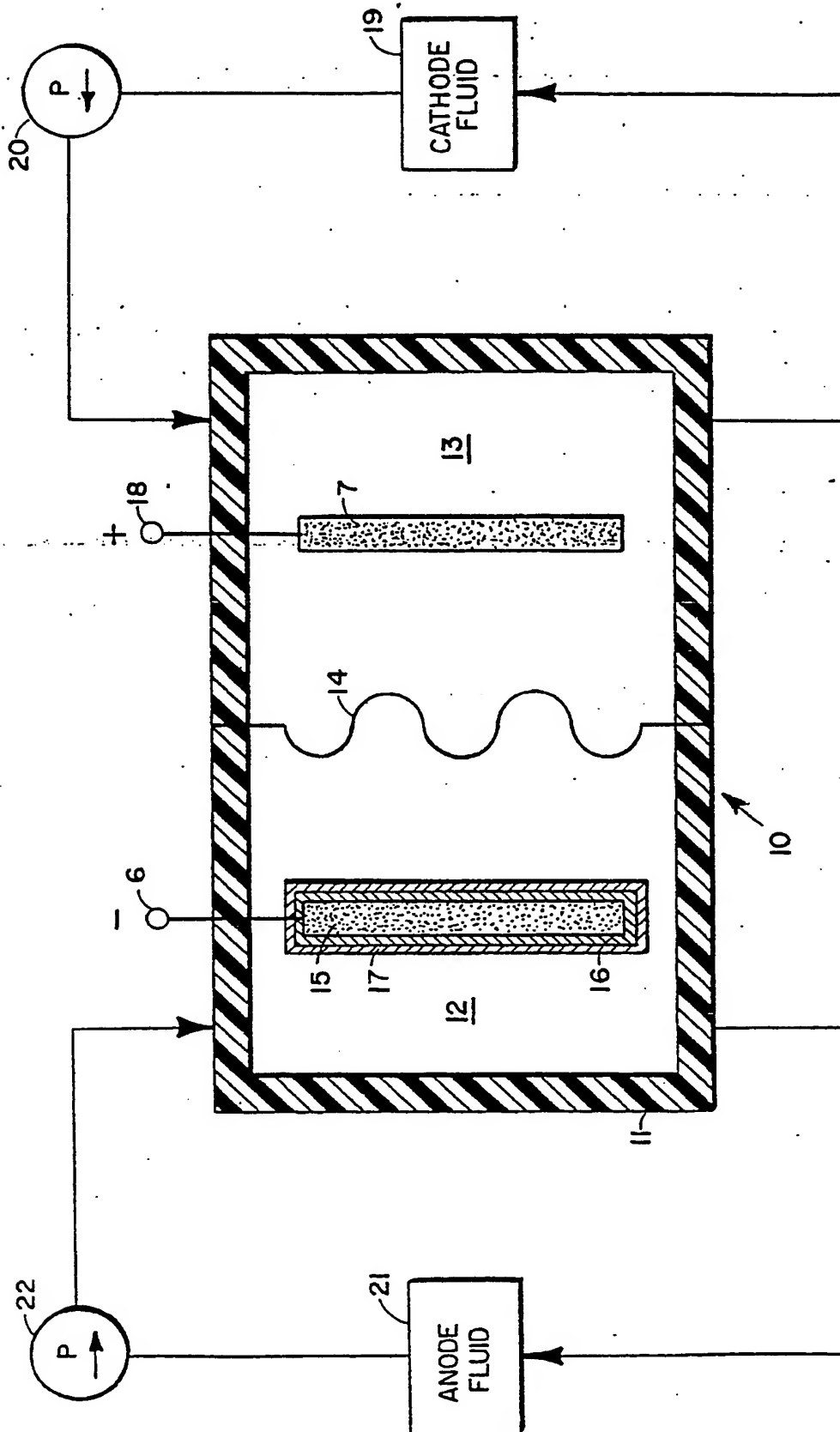


FIG. 1



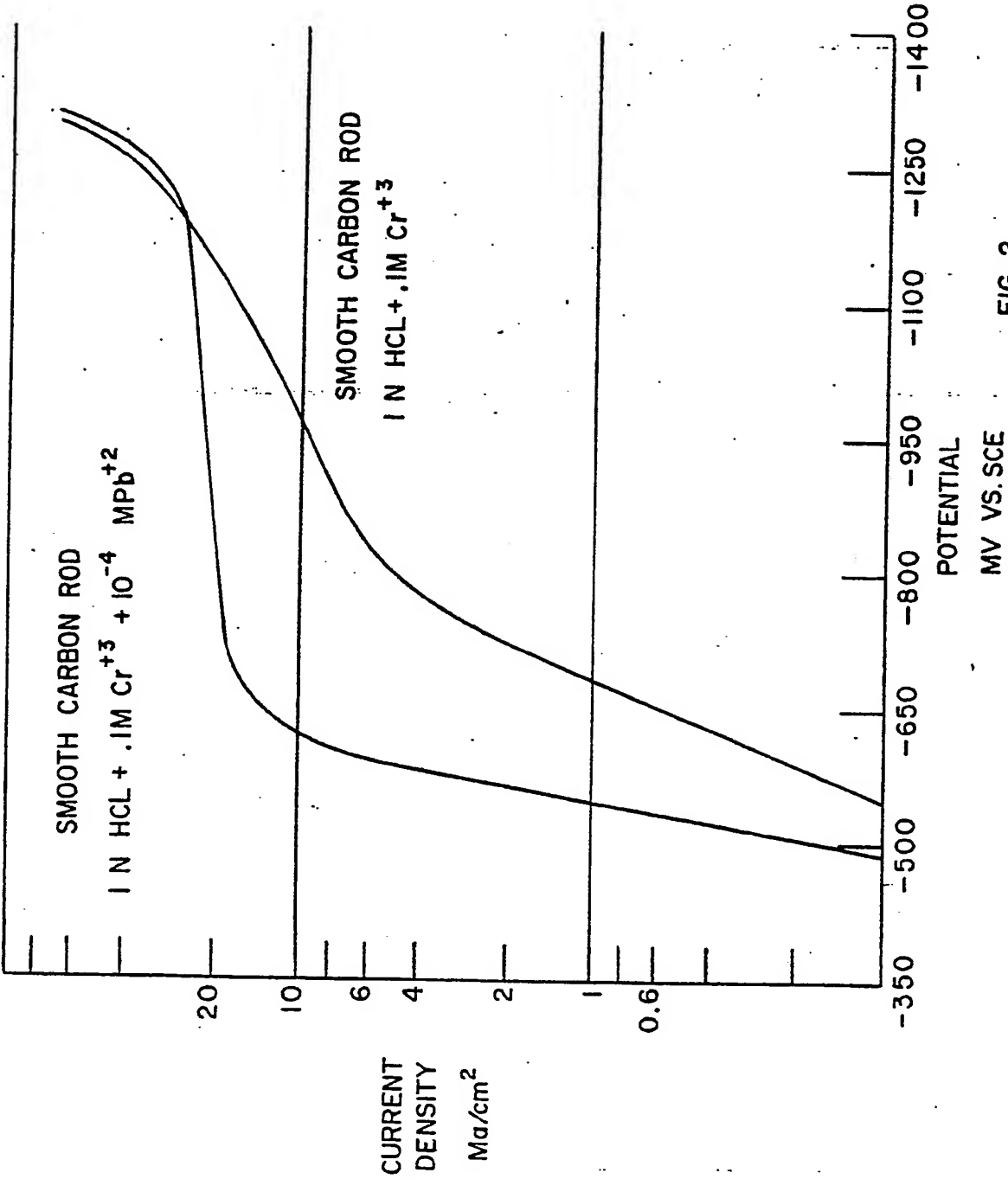


FIG. 2



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IN HCL - 0.1M CrCl_2

1. SILVER WIRE ELECTRODE
2. COPPER FOIL ELECTRODE
3. CARBON ROD ELECTRODE

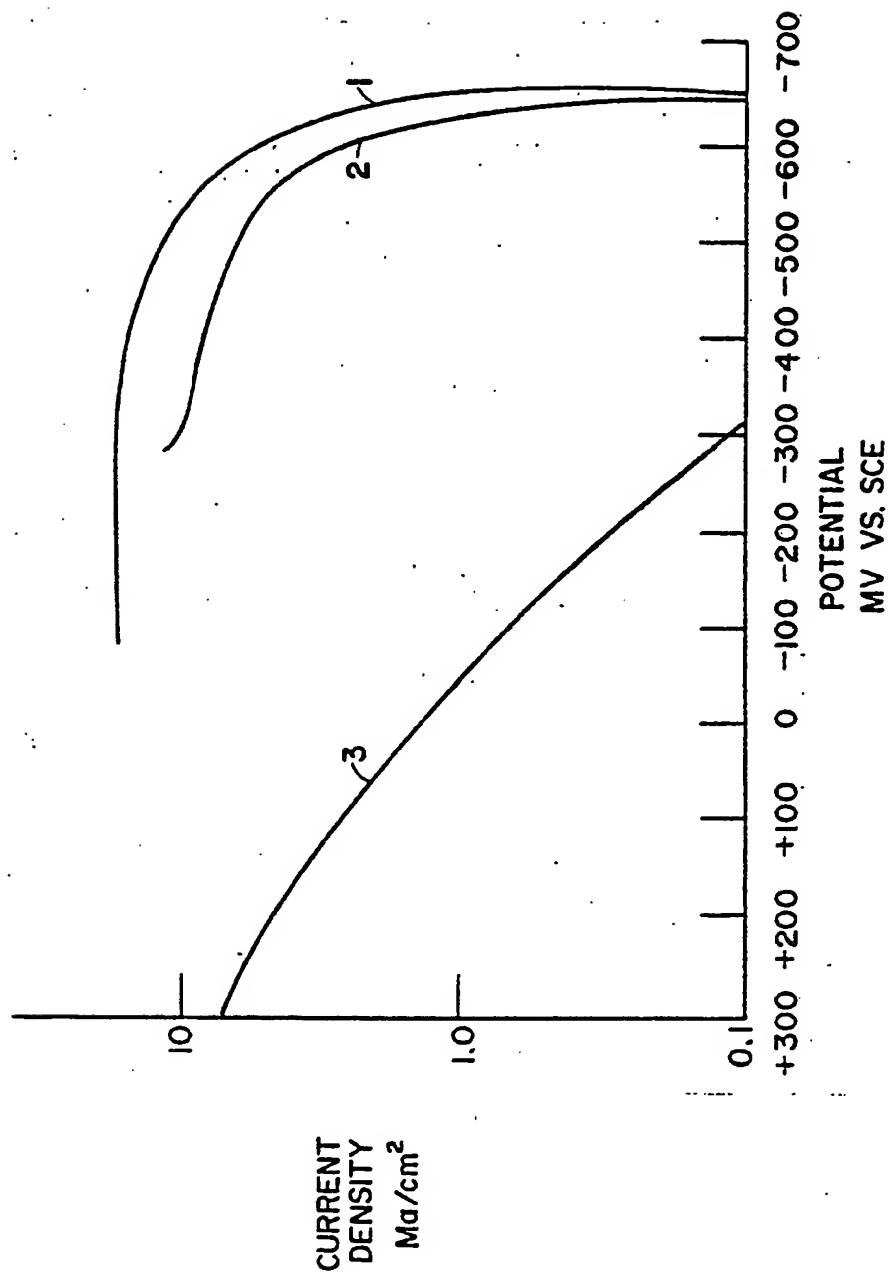


FIG. 3



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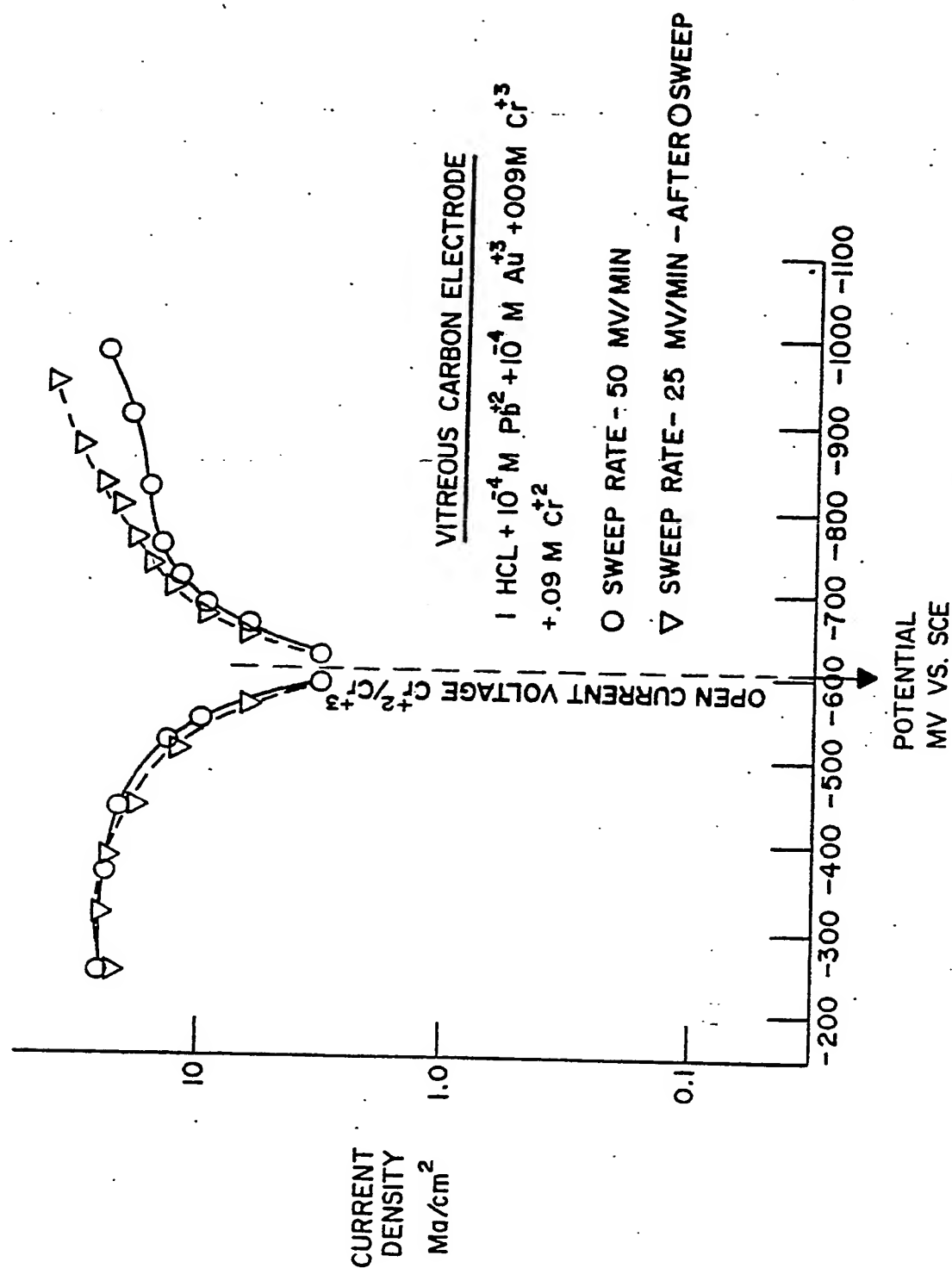
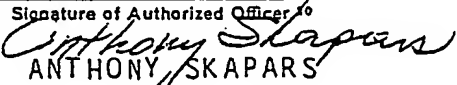


FIG. 4



INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 79/00997

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL ³ Ho1M 8/20; INT. CL ³ C 25B 11/04 US CL. 429/105 204/53		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	429/101, 105, 15, 14, 19, 17, 40, 46, 34 204/53, 50R, 52R, 46G, 292, 2.1	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁵	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US A, 3,178,315, Published 13 APRIL 1965, Worsham	
A	US A, 3,616,305, Published 26 OCTOBER 1971, Arbez	
A	US A, 3,255,046, Published 07 JUNE 1966, Ghormley	
A	US A, 3,279,949, Published 18 OCTOBER 1966, Schaeferetal	
A	US A, 3,540,934, Published 17 NOVEMBER 1970, Boeke	
A	US A, 3,920,474, Published 18 NOVEMBER 1975, Zito, Jr., et al	
A	US A, 3,996,064, Published 07 DECEMBER 1976, Thaller	
A	US A, 4,053,684, Published 11 OCTOBER 1977, Zito, Jr., et al	
* Special categories of cited documents: ¹⁵ <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </div> <div style="width: 45%;"> <p>"P" document published prior to the International filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the International filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹		Date of Mailing of this International Search Report ²
28 FEBRUARY 1980		13 MAR 1980
International Searching Authority ¹		Signature of Authorized Officer ¹⁰
ISA/US		 ANTHONY SKAPARS

801021

International Application No. PCT/US 79/00997

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A, P	US A, 4,159,366, Published 26 JUNE 1979, Thaller	
X	US A, 2,485,258, Published 18 OCTOBER 1949, Chambers et al	13-20
X	US A, 2,649,478, Published 14 MARCH 1972, Beckwith	13-20
X	US A, 3,505,182, Published 07 APRIL 1970, Pokras	13-20

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

Invention I: Claims 1-12

Invention II: Claims 13-20

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☒ No protest accompanied the payment of additional search fees.